DEMULSIFICATION OF WATER-IN-CRUDE OIL EMULSIONS VIA MICROWAVE HEATING TECHNOLOGY

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ABSTRACT

Traditional methods to separate water-in-crude oil emulsions like chemical demulsifiers are not environmentally-friendly, slow, separation not efficient, not cost effective and consume space for separation. The potentials of microwave energy in demulsification of water-in-crude oil emulsions were investigated. In this study, stability tests, gravity settling, microwave heating and microwave separation were studied. Microwave demulsification was applied in 50/50 and 20/80 water-in-crude oil emulsions with microwave exposure time varied from 120-180 seconds. As the sludge is heated, viscosity is lowered, and rapid coalescence of liquid phases takes place. Once the liquid phases coalesce, separation occurs through natural gravity. No chemicals are needed to force separation. Three different parameters were being investigated on the effect of separation namely volume ratio of water-in-oil emulsions, different emulsifiers and power generations of microwave. The four emulsifiers used were SDDS, Span 83, Triton X-100 and Tween 80. The power generations were 360 and 540 watts respectively. 20/80 water-in-crude oil emulsion was the most stable among two volume ratios. Newtonian fluid was determined from stability tests. Viscosity decreased, shear stress increased and shear rate increased over rpm. Surface and interfacial tensions were determined. Water and oil separation efficiencies via gravity settling were low. Volumetric heat generation rate of microwave was high. Water and oil separation efficiencies of microwave were more efficient than gravity settling. Microwave causes molecular rotation and ionic conduction thus fast heating.

ABSTRAK

Kaedah-kaedah tradisional untuk mengasingkan emulsi air-dalam-minyak mentah seperti agen demulsi kimia adalah tidak mesra alam, lambat, pemisahan tidak efisien, tidak jimat kos dan mengambil ruang untuk pemisahan. Keupayaan gelombang mikro dalam proses demulsi emulsi air-dalam-minyak mentah dikaji. Dalam kajian ini, ujian kestabilan, pemendakan graviti, pemanasan gelombang mikro dan pemisahan disebabkan gelombang mikro dikaji. Proses demulsi gelombang mikro diguna dalam 50/50 dan 20/80 emulsi air-dalam-minyak mentah dengan masa terdedah gelombang mikro berbeza dari 120-180 saat. Apabila kelodak dipanaskan, viscosity direndahkan, dan percantuman cepat fasa cecair mengambil tempat. Sebaik sahaja fasa cecair bercantum, pemisahan berlaku secara graviti semulajadi. Tiada bahan kimia diperlukan untuk pemisahan berlaku. Tiga parameter dikaji untuk kesan pemisahan antaranya ratio isipadu emulsi air-dalam-minyak, agen emulsi yang berbeza dan kuasa generasi gelombang mikro. Empat agen emulsi yang diguna adalah SDDS, Span 83, Triton X-100 dan Tween 80. Kuasa generasi adalah 360 dan 540 watt. 20/80 emulsi air-dalam-minyak mentah adalah paling stabil antara dua ratio isipadu. Fluid Newtonian ditentukan melalui ujian kestabilan. Viscosity menurun, daya tegang meningkat dan kadar tegang meningkat apabile rpm meningkat. Tension permukaan dan antara dua permukaan ditentukan. Pemisahan air dan minyak melalui pemendakan gravity adalah rendah. Kadar generasi pemanasan isipadu gelombang mikro adalah tinggi. Pemisahan air dan minyak gelombang mikro adalah lebih efisien daripada pemendakan gravity. Gelombang mikro menyebabkan putaran molekul dan konduksi ion kesannya pemanasan cepat.

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LIST OF ABBREVIATIONS

DLVO	: Van der Waals interaction, electrical double layer theory
R/A	: Resin to Asphaltene ratio
MPS	: Multi-Phase Separation
MESB	: Mechanical Emulsion Breaker
mw	: microwave
o/w	: oil-in-water emulsion
w/o	: water-in-oil emulsion
SDDS	: Sodium Dodecyl Sulfate
T X-100	: Triton X-100
mins	: minutes
SR	: Shear Rate
Visc.	: Viscosity

SS	: Shear Stress
rpm	: rotations per minute
hr	: hour
hrs	: hours

LIST OF SYMBOLS

50/50 or 50-50	: emulsion of 50 volume % water in 50 volume % of crude oil
20/80 or 20-80	: emulsion of 20 volume % water in 80 volume % of crude oil
v_w	: Settling velocity (cm/sec)
ρ_w	: Density of water (g/cm3)
ρ_o	: Density of oil (g/cm3)
g	: Gravity
D	: Droplet diameter (cm)
μ_o	: Viscosity
P_o	: Microwave surface power (W)
m	: Mass of sample (g)
A	: Sample container area (cm^2)
α_E	: Electromagnetic attenuation factor (cm-1)

f	: Frequency of incident microwaves
P_z	: Microwave power transmitted (W)
δ	: Loss tangent
q_{mw}	: Volumetric heat generation rate (cal/cm^3.s)
λ_m	: Wavelength (cm)
D_p	: Penetration depth (cm)
ε'r	: Dielectric constant
ε"r	: Dielectric loss
c	: Speed of light (cm/s)
h	: Convective heat transfer coefficient (cal/s.cm^2.^{o}C)
v	: Volume of water separated (cm3)
T_m	: Temperature of emulsion (^{o}C)
T_a	: Temperature of ambient (^{o}C)
σ	: Stefan-Boltzmann constant
ε	: Emissivity of surface
Cp or Cp_m	: Heat capacity of emulsion (cal/g.^{o}C)
ρ	: Density of emulsion (g/cm^3)

dT/dt	: Rate of temperature increase
ϕ	: Real water ratio inside emulsions
ρ(water) or ρ_w	: Density of water
ρ(oil) or ρ_o	: Density of oil
ρ_m	: Density of emulsion

CHAPTER 1

INTRODUCTION

1.1 Problem Statement

In many oil fields, following the initial gas-oil separation process, the oil must be treated to remove water, salt, or H_2S. Most pipeline quality oil must have its water content reduced to the 0.2% to 2% by volume range. Because salt water is generally associated with oil in the reservoir, its production along with the oil is not unusual. Almost all well streams contain water droplets of various sizes. If, because of their higher density, they collect together and settle out within a short period of time they are called free water. A more difficult separation problem arises when the oil and water are produced as an emulsion. Most oilfield emulsions are the water-in-oil type, where individual water particles are dispersed in a continuous body of oil. An inverted, or oil-in-water, emulsion can also occur, especially when the ratio of water to oil is very high. Two things are necessary to produce an emulsion of water and oil: agitation and an emulsifying agent. In order to “break” the emulsion and separate the oil from the water, a variety of processes have been developed. Conventionally, chemicals are normally added continuously to the produced fluids, as far upstream from the treating or separation facilities as possible. This is the simplest and least expensive method currently endorsed by most of the oil companies. The addition of microwave heating is necessary and economically attractive when the space for chemical addition is limited in offshore production facilities. As older fields begin to produce increasingly higher water cuts, and when water injection projects are begun in depleting fields, the need for emulsion treating processes can increase. Small amounts of water can cause problems, particularly if the salinity is high. Salty crude will cause severe problems during the refining process by producing corrosive compounds under high temperatures and depositing mineral residues within the refining equipment. Untreated water in crude oil can also cause high wastewater loads when piping to refineries. Produced water, after separation and treatment, is normally disposed of by injection into disposal wells, reinjection into the reservoir as part of a waterflood project, or pumping to open pits where it is allowed to evaporate or drain. At some offshore locations, the water may simply be pumped into the ocean [Karl, 1986]. Traditional method using chemical addition to separate water-in-crude oil emulsions will cause pollution and environmental problems whether to mainland organisms or marine aquatics. So, a better alternative has been discovered which is microwave heating. It is environmentally friendly, not space confining and time-saving.

1.2 Objectives

1. To study the separation or demulsification (breaking emulsions) of water-in crude oil emulsions via microwave heating technology.
2. Analyze the overall performance of microwave heating as an alternative method for water-in-crude oil emulsions breaking compared to chemical addition.

1.3 Scopes

In order to achieve the objectives, the following scopes have been identified:

a) Characterization of emulsions in terms of chemical and physical properties such as density, viscosity, surface tension, interfacial tension, shear stress, shear rate, rotations per minute (rpm) and temperature.
b) To examine the demulsification of water-in-crude oil emulsions via microwave heating technology using batch process system.
c) To study the effects of varying the microwave power generation at 900, 720 and 540 watts.
d) Evaluation of volume rate of microwave heat generation.
e) Comparison between microwave heating technology and conventional method (chemical addition and hot plate).
f) To evaluate temperature profile at different locations for emulsions.

1.4 Rationale & Significance

The rationale and significance of separation of water in crude oil emulsions via microwave heating method will be compared with conventional method of using chemicals.

Firstly and most importantly, microwave heating method is an environmentally friendly method. It does not cause pollution to the environment. It does not need any chemical addition to separate crude oil emulsions. Traditional and present way of using chemicals to demulsify crude oil emulsions will create polluted waste water problem.

Secondly, microwave heating method is cost effective. It does not need the purchase of large quantities of chemicals which are expensive to separate crude oil emulsions. It only requires microwave heating machine to demulsify water in crude oil emulsions. The lower cost of using microwave heating method outweighs chemical method in comparison.

Thirdly, microwave heating method is time-saving and efficient. It requires only a short period of time for the effective separation of water in crude oil emulsions. On the other side, chemical method will take a lot of time for the settling process to take place. In industrial real site, it may take at least a week to separate water in crude oil emulsions using chemical method.

Fourthly, microwave heating method is not space confining. Because it only takes a brief period for separation, space used by microwave heating method will only takes a short time for separation. Microwave heating method is necessary when the space for chemical addition is limited in offshore production facilities. Unlike microwave heating method, chemical method takes a long time for separation and eventually takes up a lot of space for storage to let separation happens.

Lastly, microwave heating method is a clean technology. It does not produce any side effect to the environment. It is energy efficient and environmentally benign. It dramatically eliminates the use of chemicals. Microwave heating method to separate crude oil emulsions is superior to the conventional chemical method. It offers significant additional benefits, notably the efficiency of separation.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Water is normally present in crude oil reservoirs or is injected as steam to stimulate oil production. Water and oil can mix while rising through the well and when passing through valves and pumps to form in most cases relatively stable dispersions of water droplets in crude oil (w/o), which are usually referred to as oilfield emulsions. The formation of emulsions creates problems during the production, transport of multiphase oil-water-gas mixture to the land based process plants from the production sites. Formation of these emulsions during oil field production is a costly problem, both in terms of chemicals used and due to production losses. To reduce the water content of the produced crude oil, the water/crude oil emulsions have to be broken (demulsified) [Abdurahman H. Nour *et al.*, 2008]. Thus, it is important to understand the mechanisms responsible for formation, stabilization and controlling of these emulsions. There are many types of methods used to demulsify water-in-crude oil emulsions such as chemical additions, membrane separations, electrical, mechanical, conventional heating and microwave heating. In this context, microwave heating method will be used to demulsify water-in-crude oil emulsions. Many parameters had been considered in the previous researches. This study enhances microwave heating technology by varying the power generation and usage of different emulsifiers and demulsifiers.

2.1.1 Background

Emulsion is a thermodynamically unstable system consists of dispersed phase scattered across continuous phase. The dispersed phase (solid or liquid) is immiscible with the continuous phase. There are two types of water-crude oil emulsions, which are water-in-oil emulsions (meaning water is the dispersed phase and oil is the continuous phase) and oil-in-water emulsions (meaning oil is the dispersed phase and water is the continuous phase). Most well reservoir produced oil type is water-in-oil emulsions.

Microwaves are electromagnetic waves with wavelengths from 1mm to 1m, or with frequency from 0.3 GHz to 300 GHz. Microwave irradiation are being studied as a tool for demulsification. This is due to the fact that microwave irradiation offers a clean, cheap and convenient heating process that in most of times results into better yields and shorter reaction times [Coutinho et *al.*, 2007].

The heating of liquids using microwaves can be explained by the interaction of matter with the electric field of the incident radiation, causing the movement of ions as well as that of induced or permanent molecule dipoles. The movement of such species can cause heat generation. The two main dielectric heating mechanisms are: dipole rotation and ionic conduction. Electric dipoles are formed by the redistribution of electric charges. The action of an electric field causes the orientation of dipole moments parallel to the electric field, while the action of an electromagnetic field results in the rotation of the dipoles caused by the high number of times that the electromagnetic field is alternated. In liquids, the electric dipoles cannot rotate instantaneously and the time required for the movement of the dipoles depend on the molecular mass, on the viscosity of the medium and on the forces exerted by the neighboring molecules. For frequencies comprised between low and very high, electric dipoles slightly delay with respect to electric field variations and a portion of the energy that the electric field provides for dipole rotation is stored. Such energy will be turned into heat resulting from the friction with neighbouring molecules. This heating mechanism is called dipole rotation. When the irradiated sample is an electric conductor or semiconductor formed by ions (such as NaCl aqueous solutions), these ions can move through the material so as to follow the variations in electric field. The resulting electrical currents heat the sample as a consequence of the electrical resistance. This mechanism is called ionic conduction [Coutinho et *al.*, 2007].

Separation occurs mainly because of coalescence, flocculation and sedimentation. Stability (instability) of an emulsion is caused by the coupling of coalescence and flocculation, which follow a multiplication principle rather than an additivity principle. This means that the total result of the application of a stabilizer (destabilizer) depends very much on both flocculation and coalescence processes [Sjöblom et *al.*, 2005].

Coalescence is the process in which two or more emulsion drops fuse together to form a single larger drop, and is irreversible as Figure 3.2 indicates. As already mentioned, for large drops approaching each other (no background electric field), the interfaces interact and begin to deform. A plane parallel thin film is formed, which rate of thinning may be the main factor determining the overall stability of the emulsion. The film thinning mechanism is strongly dependent on bulk properties (etc. viscosity) in addition to surface forces [A. Hannisdal, 2005].

Flocculation is the process in which emulsion drops aggregate, without rupture of the stabilizing layer at the interface. Flocculation of emulsions may occur under conditions when the van der Waals attractive energy exceeds the repulsive energy and can be weak or strong, depending on the strength of inter-drop forces. The rate of flocculation can be estimated from the product of a frequency factor (how often drops encounter each other) and the probability factor (how long they stay in contact). The first depends on the driving force for droplet movement whereas the latter depends on the interaction energy of the droplets [Binks, 1998]. The driving forces for flocculation can be (1) *body forces*, such as gravity and centrifugation causing creaming or sedimentation, depending on whether the mass density of the drops is smaller or greater than that of the continuous phase. Since drops of different size move with different velocities, drops are also subjected to aggregation during creaming/sedimentation. Gravitational sedimentation is used industrially in for example hydrocyclones or traditional settling tanks (2) *Brownian forces* or (3) *thermocapillary migration* (temperature gradients) may dominate the gravitational body force for very small droplets, less than 1 μm [Danov et *al.*, 2001].

The discovery of enhanced separation of oil-water emulsions and dispersions using microwave radiation was first disclosed in 1986 by Wolf, N. O. in U.S. Pat. No. 4,582,629. In this disclosure, Wolf demonstrated through several benchtop experiments that modest amounts of microwave power applied to oil-water emulsions could increase oil-water separation rates by more than a factor of two compared to simple heating alone. Results suggested that microwaves were enhancing the separation rate through a mechanism distinct from heating alone. Wolf postulated that microwaves were successful because of direct heating of the bulk of the emulsion and disruption of surfactant molecules present in the interfacial film.

Since Wolf's pioneering work, independent confirmation of his general results were obtained by several researchers. For example, Nikola *et al.*, with the support of the EPRI Center for Materials Production developed a novel apparatus for testing continuous separation of emulsions using microwave radiation. Purta found significant reduction in the time required to separate oil and water phases of emulsions using only small amounts of microwave energy and with temperature rises of only 20 degrees C.

A research report, prepared by Fang, C. S.; Chang, B. K. L.; Lai, P. M. C.; Klaila W. J. presented systematic data on the effectiveness of microwave radiation in separating water-oil mixtures and emulsified oil-water-solid sludges. The authors concluded that microwave radiation was more effective in heating thick, viscous emulsions than gas or oil-fired heaters. Enhanced emulsion breaking with microwave radiation was also reported. They found evidence that enhanced separation rates were due to reduction of the zeta potential, which suspends water droplets and solid particles in an emulsion.

Following the original disclosure of Wolf, a comprehensive series of patents were generated which disclosed novel concepts for applying microwaves to oil-water emulsions. Among these are U.S. Pat. Nos. 4,853,507; 5,055,180; 4,810,375; and 4,853,119. All of these patents assert the advantages of enhanced emulsion breaking properties through the application of microwave radiation. While generally applicable to any type of emulsion or suspension, one of the largest potential users of microwave-enhanced emulsion breaking technologies is the petroleum industry. Most of the patents referenced previously discuss applications in this specific industry.

2.2 Stability of Crude Oil

2.2.1 Mechanisms of Stabilization of Water-In-Crude Oil Emulsions

The mechanisms of stabilization of water-in-crude oil emulsions have been investigated by changing the solvent-solute interactions in crude oil. Diluting the original crude oil with varying amounts of heptane, which is a poor solvent for asphaltenes, changes the solvent-solute interactions, leading to flocculation of asphaltenes and thus changing the emulsion stability. The interactions between the water droplets in an emulsion system have been quantified by measuring the radial distribution function and thereby the pair potential using the digitized optical imaging technique. It has been observed that the force of interaction between water droplets is oscillatory. This shows that non-DLVO forces, such as attractive depletion and repulsive structural forces, exist between the droplets. The interaction between the water droplets has been modeled by studying the properties of a thin liquid film sandwiched between the water droplets. Because of the film confinement effect, asphaltene-resin particles form a layered structure inside the thin liquid film. Also, the role of hydrodynamic interactions has been studied by using the film rheometer to measure the dynamic film tension and film elasticity. It has been found that, because of the adsorption of asphaltene at the film interfaces, the film elasticity plays a significant role in stabilizing these emulsions [Kumar *et al.*, 2001).

2.2.1.1 Water-In-Crude Oil Emulsions: Its Stabilization and Demulsification

The effect of the water content, agitation speed, resin/asphaltene (R/A) ratio, surfactant concentration, and temperature on crude oil emulsion stability has been shown in past journal. For water content, lower water (v/v) in water-in-oil emulsions, a higher solids concentrations was found allowed easier emulsification and slowed the settling process. There is a correlation between dynamic viscosity and mixing speed, which is; as increasing the mixing speed, resulting in increase of the viscosity of the emulsion, which means the stability of the emulsions increases. High resin/asphaltene (R/A) ratios decrease the water-in-oil emulsion stability. The effectiveness of water-in-oil emulsion stabilization increases with increasing surfactant concentration and decreases with increasing temperature [Abdurahman H. Nour *et al.*, 2008].

The microwave heating process was examined for emulsions samples. Results of this study showed that, microwave radiation is a dielectric heating technique with the unique characteristics of fast, volumetric and effective heating is feasible and has the potential to be used as an alternative way in the demulsification of water-in-oil emulsions. From temperature distribution profiles of irradiated emulsion, it appears water-in-oil emulsions has been heated quickly and uniformly by microwaves rather than by conventional heating. This new separation technology does not require chemical addition. Furthermore, microwave radiation appears to provide faster separation than the conventional heating methods [Abdurahman H. Nour et *al.*, 2010].

I will enhance this microwave heating technology by varying the power generation, usage of different emulsifiers and demulsifiers.

Water-in-crude oil emulsion creates a lot of problems, especially foaming and corrosion in pipeline. Most of the oil companies use chemicals to demulsify water-in-crude oil emulsions, which may require additional cost and sometimes affect the chemical properties of the crude oil itself. So, to demulsify water-in-crude oil emulsions, it is required an easy, applicable, safe, cost effective method. So, I will be using microwave method in demulsification process to remove water-in-crude oil emulsions, which cause corrosion in pipelines.

2.2.1.2 Stability Investigation of Water-in-Crude Oil Emulsion

Experimental data are presented to investigate the stability of water-in-crude oil emulsions in both creaming and coalescence states were measured as a function of sodium chloride concentration. Also the stability of w/o emulsion is investigated over a wide range of parameters. These parameters are salt concentration (0-5.5%), mixing speed (800-1600 rpm), water concentration (10-80%) and temperature.

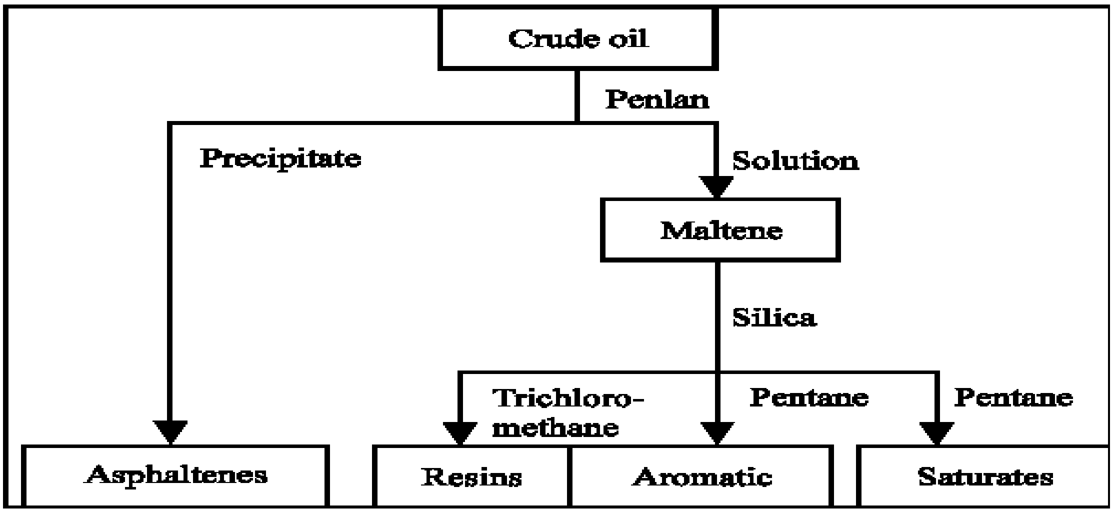

Fig 2.1: Separation of Crude Oil Fractions